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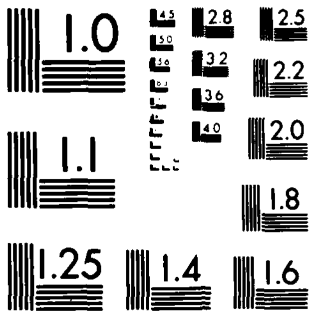

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Electrochemical Reduction of Organophosphorus Compounds
Mechanism and Products from Phosphorus-Halogen Bond Cleavage

by

T. J. Hall and J. H. Hargis

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ELECTROCHEMICAL REDUCTION OF TRIVALENT ORGANOPHOSPHORUS COMPOUNDS: MECHANISM AND PRODUCTS FROM PHOSPHORUS-HETEROATOM BOND CLEAVAGE

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Contribution from the Department of Chemistry, Auburn University, Auburn University, Alabama 36849

ABSTRACT: The cathodic cleavage at platinum electrodes of phosphorus-heteroatom bonds in fluoro-, chloro-, bromodiphenylphosphine and in phenyldiphenylphosphinite in dry acetonitrile solution has been accomplished with the formation of tetraphenyldiphosphine as the exclusive product. A mechanism which involves the intermediacy of diphenylphosphinyl anions is suggested based on cyclic voltammetry and controlled potential coulometry studies.

INTRODUCTION

The application of electrochemical techniques to the synthesis of organic compounds is an area which is rapidly developing. Relatively little attention, however, has been devoted to the study of organophosphorus compounds. We have undertaken an investigation of the electrochemical cleavage of phosphorus-heteroatom bonds in trivalent phosphorus compounds in anticipation that either the radicals, II, or anions, III, (eq. 1) which are potential intermediates might be synthetically useful.

$$(1)\quad Ph_2PX + e^- \longrightarrow Ph_2PX^{\dot{-}} \longrightarrow \underset{\text{II}}{Ph_2P^{\cdot}} + X^- \xrightarrow{e^-} \underset{\text{III}}{Ph_2P^-}$$

Ia X= Cl
Ib X= Br
Ic X= F
Id X= OPh

Dessy, et al[1] have reported that reduction of chlorodiphenylphosphine, Ia, at a mercury cathode at -3.4 V vs Ag|AgClO$_4$ in glyme resulted in the formation of diphenylphosphine (eq 2). Dessy interpreted this to result from a one electron reduction forming the diphenylphosphinyl radical, II, which subsequently abstracted hydrogen from the solvent forming product (eq 2). These

$$(2)\quad Ph_2PCl + e^- \longrightarrow Ph_2P^{\cdot} + Cl^- \xrightarrow{S-H} Ph_2PH$$

authors reported that no reversibility was detected by cyclic voltammetry using sweep rates of up to 100 V/sec.

RESULTS

We have investigated the cyclic voltammetry of Ia-Id at a platinum disk electrode in painstakingly dried acetonitrile containing tetra-n-butylammonium perchlorate as electrolyte. We have observed rather complex concentration and sweep rate dependent behavior and the peaks observed are broad and poorly defined. Additional scouting studies of the cyclic voltammograms at glassy carbon and at mercury gave completely analogous results and the results obtained were identical with and without using IR compensation. Figure 1 shows cyclic voltammograms of Ia and Ib at platinum. At the lowest concentration investigated, 6.7 mM, and at scan rates of 100 mV/sec both Ia and Ib exhibited two reduction waves. In the case of Ia these included a broad peak at -0.95 V (vs Ag|Ag+) and another at -2.92 V. The first wave was not reversible through the highest scan rates investigated, 500 mV/sec. The second wave was quasi-reversible with the anodic Ep at -2.79 V. A small second oxidation peak was observed at -0.63 V. Completely analogous behavior was observed for Ib, Ic, and Id under identical conditions. Peak potentials for all four compounds are tabulated in Table I. At higher concentrations the first cathodic peak moved to more negative potential and broadened dramatically. For Ia at 100 mV/sec the peak maxima occurred at -0.97, -1.38, -1.41, and -1.47 V at concentrations of 0.0067, 0.0134, 0.0268, and 0.0534 Molar, respectively. This peak also moved to more negative potential with increasing scan rate and plots of i_p vs the square root of the sweep frequency are linear over the entire range of concentrations studied. Figure 2 illustrates this relationship for compounds Ia-Id. The peak current also varied as a function of the concentration, but not linearly. Figure 3 illustrates this behavior for compound Ia; similar behavior was observed for the other compounds. At the higher concentrations the current was lower than would have been predicted if a linear dependence was obeyed.

The observed Ep's for the first reduction in each compound were observed to shift to more negative potential as the leaving group was varied from Br to Cl to F to phenoxy.

All four compounds exhibited a second reduction peak which was quasi-reversible and within the limits of experimental error these peaks occurred at the same potential. A complete tabulation of these data can be found in Table 1.

Compounds Ia and Ib also exhibited another interesting oxidation peak. If a normal scan starting at 0.0 V was stopped at -1.6 V and held at this potential for a period of time and then reversed, an intense peak was observed at -1.0 V. On a subsequent normal cycle (0.0 to -3.0 V and then reversing) this peak was either very small or not observed. The current of an oxidation peak at -0.63 V was however enhanced under these conditions.

A controlled potential electrolysis at -1.6 V (vs Ag|Ag+) was performed with 0.004 moles of Ia in 200 ml of dry acetonitrile, containing tetra-n-butylammonium bromide (0.1 Molar) as electrolyte, at a monel electrode in a flow cell with a microporous glass separator. The current dropped below the original background current after passage of 396 coulombs which corresponds to a one electron reduction. A single product was obtained on workup of the solution and was identified by comparison of gas chromatographic retention times with those of a commercial sample and by ^{31}P nmr as tetraphenyldiphosphine. Gas chromatographic analysis indicated that a 92% yield of product was obtained. The cyclic voltammogram of this product exhibited a quasi-reversable peak at approximately -2.9 V and a weak oxidation wave at -0.63 V was also observed. These peaks correspond to those observed in the cyclic voltammograms of Ia-Id.

DISCUSSION

These data are interpreted to arise from the reaction processes shown in equations 3-5. Equation 3 illustrates the process resulting from the first reduction wave which occurs at -0.97 V and -0.87 V for Ia and Ib, respectively at 6.7 mM and at a sweep frequency of 100 mV/sec. The reaction is not reversible because of the rapid, or simultaneous, cleavage of the phosphorus-halogen bond yielding the diphenylphosphinyl radical, II. EC type reactions in which the following chemical reaction is fast are characterized by cyclic voltammograms in which a plot of i_p vs the square root of the sweep frequency is linear[2], and in which the Ep's observed shift to more negative potential with increasing sweep frequency[3]. All four compounds exhibit this behavior (See Figure 2 and Table 1). It is interesting to note that the slopes of these plots increase with increasing leaving group ability of the substituent X, i.e. Br>Cl>F>OPh[4]. It would be expected that the greater the rate of the subsequent cleavage reaction the greater influence a faster scan rate would have on the observed current.

$$(3)\quad Ph_2PX + e^- \longrightarrow Ph_2PX^- \longrightarrow \underset{\text{II}}{Ph_2P^{\cdot}} + X^-$$

$$(4)\quad Ph_2P^{\cdot} + e^- \longrightarrow \underset{\text{III}}{Ph_2P^-}$$

$$(5)\quad Ph_2P^- + Ph_2PX \longrightarrow \underset{\text{IV}}{Ph_2P\text{-}P_2Ph} + X^-$$

These observations do exclude another plausible mechanism[5] which is shown in equations 6 and 7. A chemical step (eq. 6) preceding the electrochemical reaction, i.e. a CE mechanism, results in cyclic voltammograms in which Ep shifts anodically with an increase in sweep frequency[6], which is not in accord with our observations (Table 1).

(6) $2\ Ph_2PCl \longrightarrow Ph_2(Cl)P^+{-}PPh_2 + Cl^-$

(7) $Ph_2(Cl)P^+{-}PPh_2 + e^- \longrightarrow Ph_2(Cl)\dot{P}{-}PPh_2 \xrightarrow{e^-} Ph_2P{-}PPh_2 + Cl^-$

Equation 4 proposes the reduction of the phosphinyl radical to the corresponding anion. If this reduction takes place at a potential positive or at approximately the same as that of the first reduction a second reduction wave will not be observed. This has been observed in the possibly analogous carbon system[7]. The appearance of the large transient oxidation wave at - 1.0 V which is observed to grow when the potential scan is stopped and maintained at - 1.6 V before rapidly scanning anodically can be attributed to the oxidation of the anion back to the corresponding radical, i.e. the reverse of equation 4. This peak is not observed in a normal cyclic voltammogram, presumably because of the very short lifetime of the anion intermediate (vide infra).

Another possible mechanism for the formation of the phosphinyl anion would be a two electron transfer which could result in the formation of the anion without involving the intermediacy of the radical. Our data cannot distinguish between these possibilities.

Equation 5 proposes that the biphosphine product could arise from attack of III on the starting material; this does indeed occur in the alkali metal induced synthesis of the biphosphine from Ia.[8] The cyclic voltammetry data also supports formation of product in this manner. Figure 3 illustrates the relationship between current and concentration for the first reduction wave. An increase in concentration does not result in the increase in current that would be expected on the basis of a linear relationship. This is consistent with a mechanism in which a single diffusion process decreases the starting material by more than one molecule. Equations 3 through 5 are compatible with this expectation, since the phosphinyl anion which is formed reacts with a second molecule of starting material thus decreasing the concentration gradient of starting material reaching the electrode surface. Our coulometry measurements are in accord with a one electron per molecule consumption of starting material or two electron transfers per molecule of product formed.

The observations discussed above argue against another possible mechanism for the formation of the dimer product. The formation of phosphinyl radicals, equation 3, and their subsequent dimerization, equation 8, could account for the formation[9] of compound IV and is in accord with our observed coulometry. We would expect that this process would require a linear relationship between current and concentration since both radicals would have to be formed from diffusion to the electrode surface. We also were not able to detect any trapping products when cyclohexene was included in the reaction mixture.

(8) $2\ Ph_2P^{\cdot} \longrightarrow Ph_2P{-}PPh_2$

The quasi-reversible reduction peak observed in the cyclic voltammograms of all four compounds at approximately -2.96 V also appears in the cyclic voltammogram of IV and thus may be assigned to the reactions shown in equation 9.

(9) $Ph_2P{-}PPh_2 + e^- \qquad Ph_2P{-}PPh_2^{\dot{-}}$

The small anodic wave observed at -0.63 volts is also observed in the cyclic voltammogram of IV as a small peak. We observe a much larger peak at this potential in the cyclic voltammogram of diphenyl phosphinic acid, Ph_2PO_2H. We thus attribute this oxidation process to result from impurities or from products resulting from the reaction of adventitious oxygen with either our starting material or intermediates formed in the reduction process. The oxidation of some substituted derivatives of tetraphenyldiphosphine to the corresponding radical cations have recently been reported[10] to occur at approximately + 0.6 volts.

We have attempted to trap the anionic intermediate in this reaction without success. The inclusion of a ten-fold molar excess of benzyl bromide in the electrolysis reaction mixture of compounds Ia-d did not result in trapping of the anion, i.e. no formation of benzyldiphenylphosphine was observed even when the leaving group was phenoxy (Id). We conclude that the starting materials are significantly better substrates for nucleophilic attack than is benzyl bromide. It is interesting to note that we have observed a product that would have been expected had the intermediate anion been trapped. If the electrolysis reaction mixture containing benzyl bromide but which had been completely converted to the diphosphine product was allowed to stand overnight white crystals were formed. Analysis of this product by ^{31}P nmr and the subsequent independent synthesis proved that the product was dibenzyldiphenylphosphonium bromide. We also found an equivalent amount of bromodiphenylphosphine in the supernatent liquid. A subsequent reaction using commercial tetraphenyldiphosphine demonstrated that the reaction shown in equation 10 was operative. A similar reaction has been previously reported in the literature.[11] We propose the mechanism detailed in equations 11 through 13 to account for the formation of these products.

(10) $Ph_2P\text{-}PPh_2 + 2\ PhCH_2Br \dashrightarrow (PhCH_2)_2P^+Ph_2\ Br^- + Ph_2PBr$

(11) $Ph_2P\text{-}PPh_2 + PhCH_2Br \dashrightarrow Ph_2P\text{-}P^+Ph_2(CH_2Ph)\ Br^-$

(12) $Br^-\ Ph_2P\text{-}P^+Ph_2(CH_2Ph) \dashrightarrow Ph_2PBr + Ph_2P\text{-}CH_2Ph$

(13) $Ph_2P\text{-}CH_2Ph$ + $PhCH_2Br$ ----> $Ph_2P^+(CH_2Ph)_2\ Br^-$

EXPERIMENTAL SECTION

^{31}P NMR's were obtained on a Varian CFT 20 instrument and are reported using the standard convention of shifts downfield of external 85% H_3PO_4 being positive.

CHLORODIPHENYLPHOSPHINE,Ia, was used as obtained from Aldrich Chemical Company. The purity was checked by ^{31}P nmr in which a single peak at +81.9 ppm ($CDCl_3$) was observed.

BROMODIPHENYLPHOSPHINE,Ib, was synthesized[12] from the reaction of 0.09 moles of chlorodiphenylphosphine with 0.19 moles of phosphorus tribromide, followed by a vacuum distillation which gave 18.3 grams (72%) of product which boiled at 130-135 @ 0.15 torr, ^{31}P nmr +72.1 ppm ($CDCl_3$), lit.[13] +70.8 ppm.

FLUORODIPHENYLPHOSPHINE, Ic, was synthesized[14] from the reaction of 0.09 moles of chlordiphenylphosphine with 0.67 moles of sodium fluoride in acetonitrile, followed by a vacuum distillation. Fifteen grams (82.5%) of product was isolated at 127-133 @ 0.01 torr, ^{31}P nmr +169.1 ppm ($CDCl_3$), lit.[14] +168.4 ppm.

PHENYLDIPHENYLPHOSPHINITE, Id, was synthesized by the dropwise addition of a solution containing 0.11 moles of phenol and 0.11 moles of triethylamine in 200 ml of ether to a 500 ml solution of 0.11 moles of chlorodiphenylphosphine in ether. Following filtration and removal of the ether, 2.3 grams (73%) of product was obtained by vacuum distillation at 183-189 @ 0.6 torr, ^{31}P +110.8 ppm ($CDCl_3$); mass spectrum, m/z 278.0856 (M^+, calcd for $C_{18}H_{15}OP$ 278.0857).

TETRA-n-BUTYLAMMONIUM BROMIDE was purchased from Aldrich Chemical Company and purified by recrystallization from benzene-hexane and dried under vacuum[15].

ACETONITRILE was purified by drying over phosphorus pentoxide for at least 24 hours before distilling and storing over 3A molecular sieves[16].

Cyclic voltammograms were obtained at room temperature on a Princeton Applied Research Model 173 Potentiostat in combination with a Model 175 Universal Programmer and recorded on a PAR Model 9002A X-Y Recorder. The cell[17] consisted of a Pt foil disk working electrode 7mm in diameter surrounded by a Pt wire coil as the counter electrode. The reference electrode was a Ag wire in 0.1 Molar silver nitrate in acetonitrile and separated from the reaction chamber by a Vycor microporous frit and in communication with the working electrode through a Luggin capillary terminating within 2 mm of the working electrode. Dry acetonitrile solutions of 25 ml containing 0.1 molar tetra-n-butylammonium perchlorate were added to the cell and flushed with dry nitrogen. Background CV scans were run to insure that no electrochemical activity was present and then the appropriate amount of compound (Ia-Id) was added via a 100 1 syringe.

The preparative electrolyses and coulometry experiments were carried out with an ECO Model 550 Potientiostat equipped with a ECO Model 721 Digital Coulometer. The electrochemical cell consisted of an ECO Model 1000 Electroprep Cell equipped with a Monel cathode and a ruthenized titanium anode separated by a microporous glass separator. The reference electrode was a Ag wire in 0.1 molar silver nitrate in acetonitrile separated from the catholyte by a microporous Vycor frit. In a typical experiment the anolyte solution consisted of 200 ml of dry acetonitrile containing 0.1 molar tetra-n-butylammonium bromide as electrolyte. The catholyte consisted of 200 ml of the above solution plus 0.882 grams (0.004 moles) of chlorodiphenylphosphine. The anolyte and catholyte solutions were circulated from separate flasks by ECO Model 920 Teflon Pumps and were continuously flushed with dry nitrogen. Yields were calculated by adding triphenyl phosphine as an internal standard and subjecting the resulting solution to gas chromatographic analysis on a 5 foot x 1/8 inch 3% SE30 on 80-100 mesh chromasorb WHP column at 215 . The detector response had been calibrated by an authentic sample of tetraphenylbiphosphine[18]. Tetraphenylbiphosphine was isolated by removing the solvent in vacuuo, dissolving the resulting oil in benzene and running this solution through a short silica gel column to remove the electrolyte salt, followed by recrystallization from benzene-hexane, mp 121 , lit.[19] 122 , ^{31}P nmr -14.4 ppm (DMSO-d-6). The isolated material was compared with authentic tetraphenylbiphosphine by observing identical gas chromatographic retention times and by spiking the isolated sample with authentic material and observing only a single peak. This spiking technique was also used in ^{31}P nmr analysis with the observation of only one resonance.

ACKNOWLEDGEMENT

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Figure 1. Cyclic voltammograms. A: Compound Ia; B: Compound Ib. Concentration 0.0134 Molar in acetonitrile containing 0.1 M tetra-n-butylammonium bromide. Sweep rate 200 mV/sec. Reference electrode $Ag|AgNO_3$.

Figure 2. Dependence of cyclic voltammetric current on the square root of sweep frequency for compound Ia-Id. Ia (0.0134 M); Ib (0.0134M); Ic (0.0134 M); Id (0.015 M)

Figure 3. Dependence of cyclic voltammetric current on concentration of compound Ia. 100 mV/sec; 200 mV/sec; 500mV/sec.

Table 1. Cyclic Voltammetric Data for 1a-1d

$E_p^a (i)^b$

	Concentration	R_1	R_2	O_1	O_2
1a					
	.0067[c]	-0.97 (50)	-2.94	-2.80	-0.63
	.0134[c]	-1.38 (85)	-2.96	-2.76	-0.60
	.0268[c]	-1.41 (155)	-3.04	-2.82	-0.64
	.0534[c]	-1.47 (250)	-2.90	-2.87	-0.66
	.0067[d]	-1.02 (70)	-2.97	-2.78	-0.64
	.0134[d]	-1.50 (120)	-2.98	-2.78	-0.61
	.0268[d]	-1.56 (220)	-3.10	-2.80	-0.65
	.0534[d]	-1.45 (355)	-2.91	-2.54	-0.67
	.0067[e]	-1.13 (110)	-3.00	-2.76	-0.63
	.0134[e]	-1.60 (185)	-3.00	-2.78	-0.57
	.0268[e]	-1.88 (325)	-3.15	-2.77	-0.66
	.0534[e]	-1.87 (550)	-3.09	-2.52	-0.65
1b					
	.0067[c]	-0.87 (60)	-2.94	-2.54	- .68
	.0134[c]	-1.02 (90)	-2.95	-2.82	- .66
	.0268[c]	-1.50 (180)	-2.76	-2.58	.....
	.0134[d]	-1.32 (125)	-2.97	-2.77	.....
	.0268[d]	-1.56 (245)	-2.79	-2.56	- .63
	.0134[e]	-1.42 (195)	-3.00	-2.74	- .66
	.0268[e]	-1.68 (380)	-2.87	-2.57	- .66
1c					
	.0067[c]	-1.64 (40)	-2.84	-2.70	- .66
	.0134[c]	-1.80 (45)	-2.88	-2.69	- .63
	.0067[d]	-1.80 (55)	-2.85	-2.71	- .66
	.0134[d]	-2.07 (65)	-2.90	-2.69	- .69
	.0067[e]	-1.98 (80)	-2.88	-2.66	- .63
	.0134[e]	-2.32 (100)	-2.93	-2.66	- .66
1d					
	.0150[c]	-1.80 (15)	-2.88	-2.61	....
	.0300[c]	-2.26 (100)	-3.00	-2.73	- .63
	.0150[d]	-2.14 (22)	-2.89	-2.61	- .60
	.0300[d]	-2.34 (140)	-3.00	-2.72	- .61
	.0150[e]	-2.40 (40)	-2.94	-2.68	....
	.0300[e]	-2.47 (220)	-3.05	-2.73	- .57

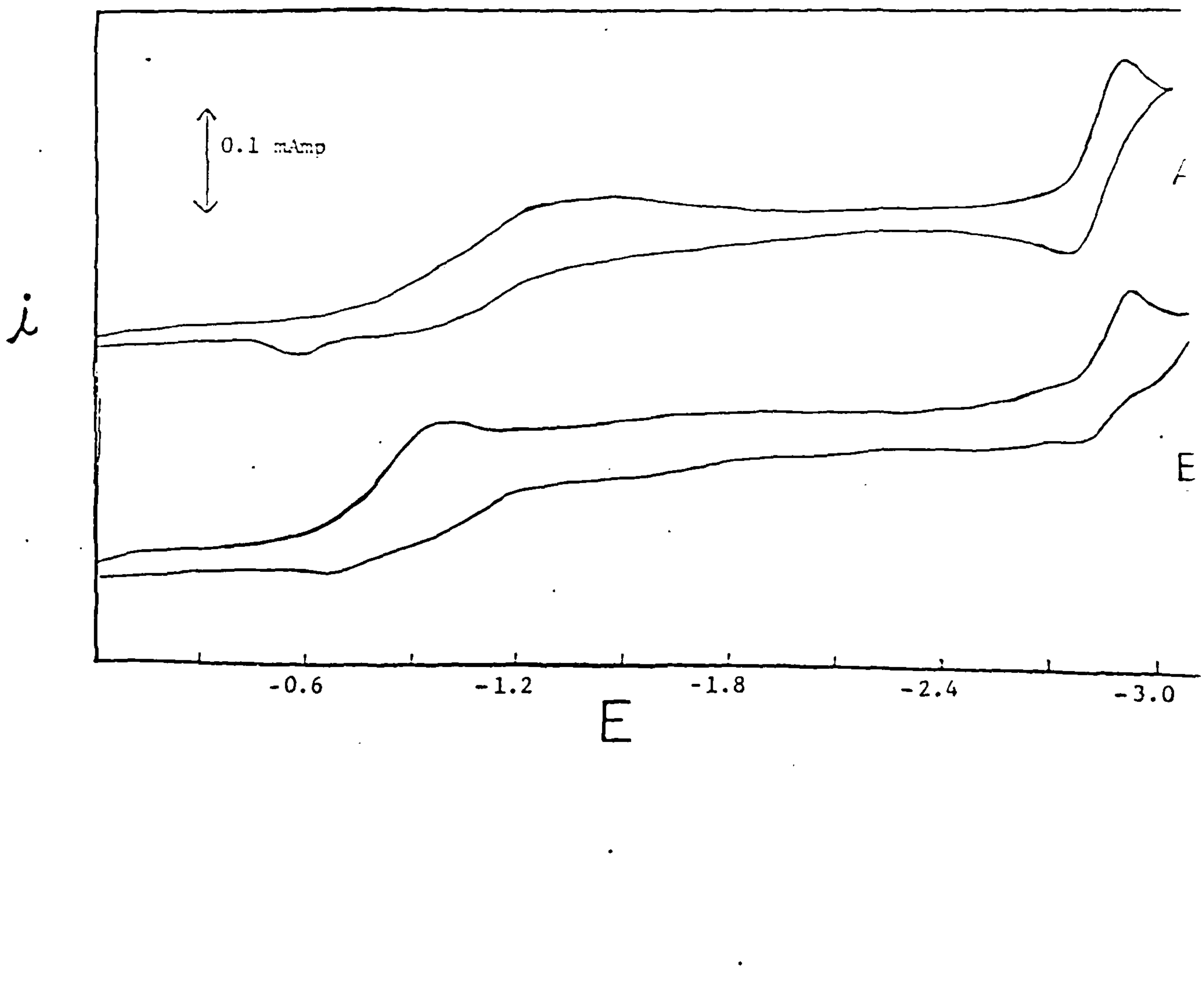
(a) V vs Ag/Ag^+ (b) μAmps (c) 100mV/sec (d) 200mV/sec (e) 500mV/sec

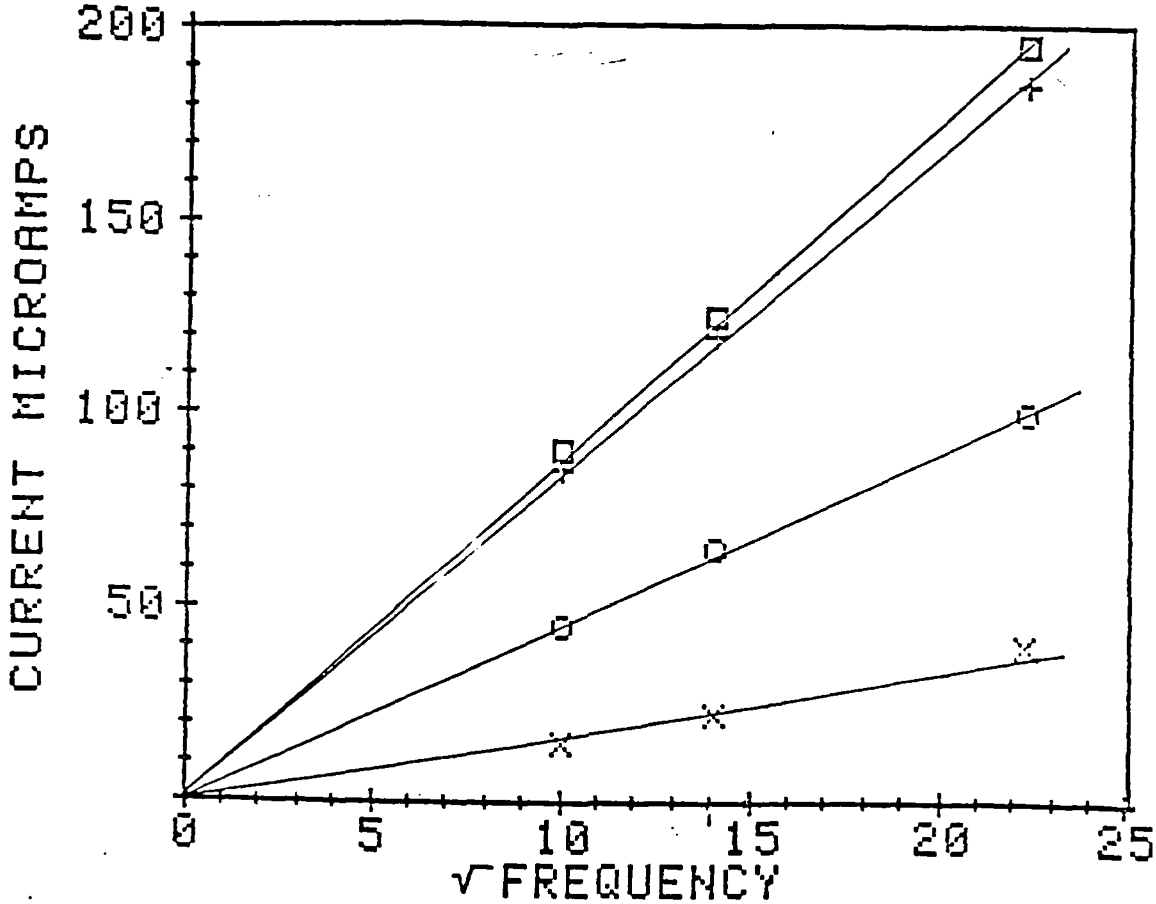
Figure 1. Cyclic voltammograms. -A: Compound Ia; B: Compound Ib. Concentration 0.0134 Molar in acetonitrile containing 0.1 M tetra-n-butylammonium bromide. Sweep rate 200 mV/sec. Reference electrode Ag|$AgNO_3$.

Figure 2. Dependence of cyclic voltammetric current on the square root of sweep frequency for compound Ia-Id. + Ia (0.0134 M); □ Ib (0.0134M); ○ Ic (0.0134 M); × Id (0.015 M)

Figure 3. Dependence of cyclic voltammetric current on concentration of compound Ia. + 100 mV/sec; × 200 mV/sec; □ 500mV/sec.

Figure 1.





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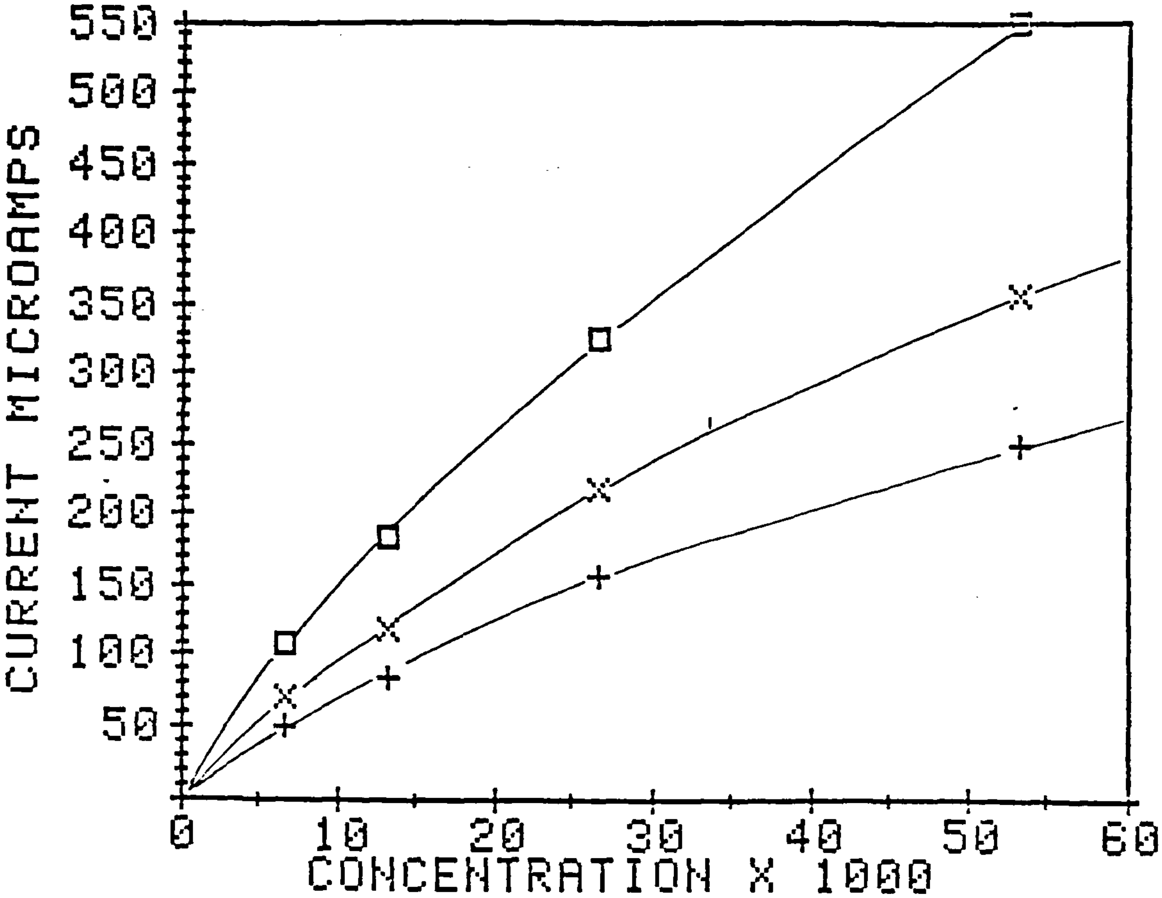

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